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Analysis

Polyisoprene Matrix Inhomogeneity Studied by Nitroxide Spin Probe Motion

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SUMMARY

The spin probe ESR method was applied to study natural rubber and synthetic polyisoprenes with different content of cis-configuration over a wide temperature range. The ESR spectra of natural rubber near and above the glass transition indicate the existence of two distinctly different mobilities as a consequence of the spin probe distribution in sol and gel phase. The results show that the spin probe method can yield information about the inhomogeneity of the polyisoprene matrix and the character of gel phase.

INTRODUCTION

It is known that natural rubber and its synthetic analogues exhibit some differences in processing in spite of the similarities in their sequence structure. Most of the differences are attributed to the inhomogeneity of the material described as sol-gel composition (MORTON 1973). Sol-gel formation and characterization have been the subject of numerous investigations.

The usefulness of the spin probe and spin label method in the study of polymer inhomogeneity has been already demonstrated (BERLINER 1979, KUSUMOTO et al. 1976, BULLOCK et al. 1983). In this article the spin probe method was applied to explore the differences in homogeneity of natural rubber and synthetic polyisoprenes and to interpret the structure of gel phase through the rotational mobility of the incorporated nitroxide probe in the polyisoprene matrix.

EXPERIMENTAL

Natural rubber (NR) (Malaysian rubber) and two synthetic polyisoprenes, Ti-catalyzed (PI-Ti) (Natsyn 2200, Goodyear) and Li-catalyzed (PI-Li)(Cariflex IR 307, Shell) polyisoprene were investigated without further purification.

Configurational parameters of the investigated polyisoprenes were determined by ^{13}C NMR spectroscopy:

	cis-1,4 %	trans-1,4 %	3,4 %
Natural rubber	98	0	1-2
PI-Ti catalyzed	97	0	2-3
PI-Li catalyzed	91	5	4

The nitroxide free radical 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl as spin probe (less than 0.1 wt%) was incorporated into the polyisoprene matrix by swelling the polymer in a benzene solution of the probe for 12 hours at room temperature. The solvent was then carefully evaporated and the samples anealed in a vacuum for several days until no change were observed in the ESR spectra. In order to examine the influence of the inhomogeneity of polymer matrix on the mobility of the spin probe the same polyisoprene samples were masticated in a Brabender Plasticorder equipped with mixer head. The mixer conditions were adjusted to bring the sample viscosity to 30 Mooney. The samples were doped following the former procedure.

Sol and gel phase in NR and PI-Ti samples were isolated by extraction in hexane. The spin probe was introduced into the separate fractions.

The ESR spectra of the spin probed polyisoprenes were recorded on a Varian E-109 spectrometer with 100 kHz modulation. The modulation amplitude and microwave power level were adjusted well below saturation and distortion of the spectra. The separation between the outermost maxima ($2A_{zz}$) of the ESR spectrum was determined from at least two recorded spectra. Near the glass transition region the samples were equilibrated for 30 min before recording.

RESULTS AND DISCUSSION

Representative ESR spectra of spin probed NR and PI-Ti observed in a wide range of temperature are given in Figure 1. The differences in line shapes of the two samples became noticable as the temperature approaches the glass transition (-20°C) and above the transition over a range of temperatures.

Spin probed NR in the transition region exhibits a composite spectrum. The separation of the outer maxima ($2A_{zz}$) is slightly reduced with the temperature increase when compared with the motionally slowed spectrum at -120°C. The composite spectrum is considered to be a superposition of two components: the broad component characteristic for the slow motion of nitroxide, and

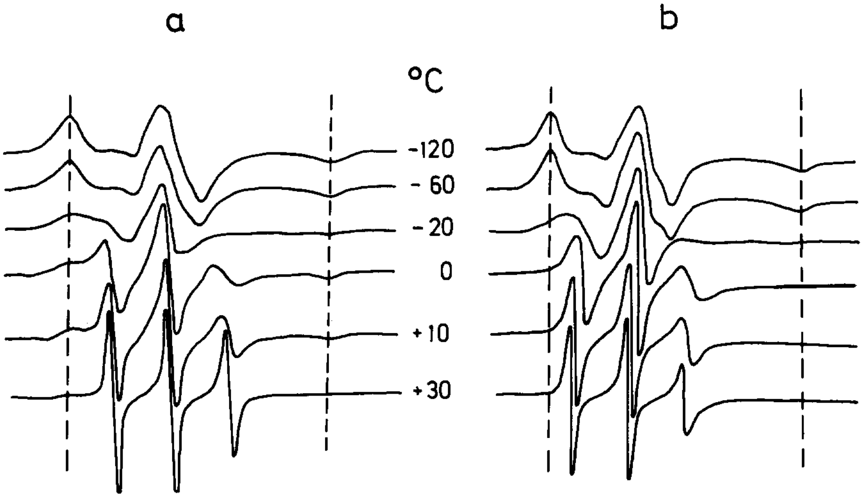

Figure 1. The temperature dependence of the ESR spectra of (a) spin probed natural rubber (NR) and (b) Ti-catalyzed polyisoprene (PI-Ti).

the narrow component which corresponds to the nitroxide population of the greater rotational mobility. The simulated spectrum consisting of two non-interconverting nitroxide motions with correlation times of $7 \cdot 10^{-10}$ s and $7.8 \cdot 10^{-8}$ s respectively, with 30% of the slow component, is very similar to the ESR spectrum of NR recorded at 10^{0}C (Figure 2).

However, the percentage of the broad component is related to the temperature and its intensity continuously decreases with temperature. This decrease is attributed to the increase of a fraction of NR free volume above the transition.

The superposition of two spectral components has in some polymer systems been interpreted as the inhomogeneity of polymer matrix (KUSUMOTO et al. 1976, BULLOCK et al. 1983) or generally, as the result of free volume (TSAY et al. 1982). The spectral changes of the synthetic polyisoprenes PI-Ti (Figure 1b) and PI-Li are very similar at various temperatures and do not exhibit composite spectra in the transition region. It should be noted that all the investigated polyisoprenes were amorphous as determined by the X-ray analysis.

To trace the origin of a double population of the nitroxide motion or inhomogeneity of the polymer matrix two additional experiments were made: the mastication and isolation of sol and gel phase. It is known that the masti-

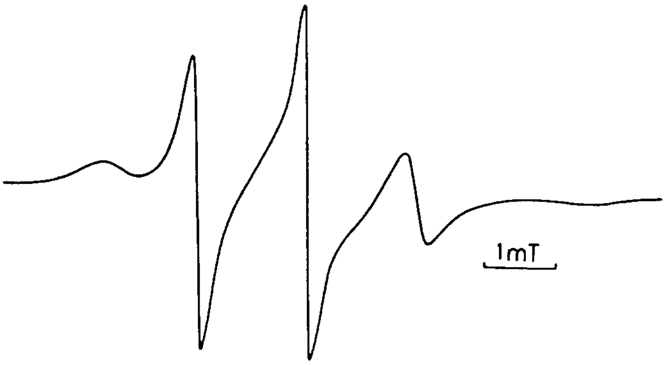

Figure 2. Simulated ESR spectrum for two noninterconverting spin probe motions.

cation reduces viscosity of polyisoprene and increases homogeneity of the structure (MORTON 1973). The structure of polyisoprene is very complex due to the possibility of branching and gel formation. Natural rubber and PI-Ti synthetic material with a high content of 1,4 sequences normally contain a varying degree of gel fraction. The gel content of NR is usually higher than that of PI-Ti polyisoprene and is probably of different structure.

The ESR spectra of masticated NR reveal similar superposition as the original sample. However, the intensity of the broad component is considerably lower when compared with the original NR sample. The line shapes of masticated synthetic polyisoprenes remained unchanged.

The spin probed isolated phases oh NR show a composite spectrum of the gel phase and a single three line component of the sol phase in the transition region (Figure 3).

Furthemore, the dominant feature of the temperature dependent spectrum of gel phase is a superimposed spectrum as in the case of the original NR. The spin probe motion appears to be sensitive to a gel structure, usually known as "loose" and "tight" gel. The line shapes of the probed sol phase within the temperature range show a single line change similar to the synthetic polyisoprenes (Figure 1b). Therefore, the broad component of the superimposed NR spectra is a result of the nitroxide probe distribution in the gel phase in which the probe motion is considerably restricted in comparison with the rapidly tumbling nitroxides in the sol phase or in "loose" gel.

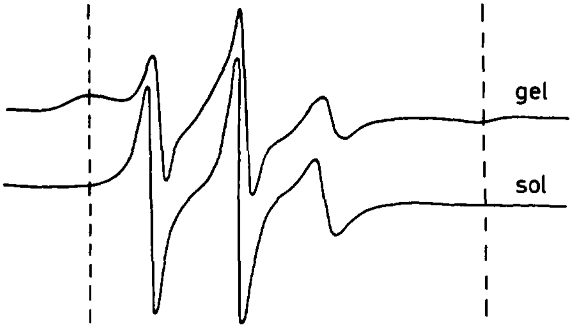

Figure 3. The ESR spectra of gel and sol phase at 10°C. The vertical lines correspond to $2A_{zz}$ of NR at -120°C.

The existence of two phases in PI-Ti samples found by the extraction experiments is not apparent in the ESR spectra. According to the spin probe method PI-Ti is considered to be homogeneous, thus suggesting that the size of the nitroxide molecule is small when compared to the gel "density" in synthetic polyisoprene contrary to the more dense NR gel ("tight gel"). At least a part of NR gel seems to have smaller internal holes in which the trapped nitroxide molecule is motionally restricted.

Although the comprehensive work on temperature dependent molecular motions of various probes in NR was published (KOVARSKY et al. 1971) our measurements of T_g from ESR spectra (Figure 4) reveal the influence of the sequence structure and inhomogeneity on the transition temperature. It is obvious that the unchanged broad component in NR is present up to 70°C. In spite of the higher T_g values in comparison with the DSC measurements (KUMLER and BOYER 1976), a shift of T_g to lower temperatures of the synthetic polyisoprene with higher degree of trans content is similar to the recent DSC results (BURFIELD and LIM 1983).

These results, although in the preliminary stage, demonstrate the possibility of spin probe method for determining inhomogeneity of the polymer matrix in terms of gel structure.

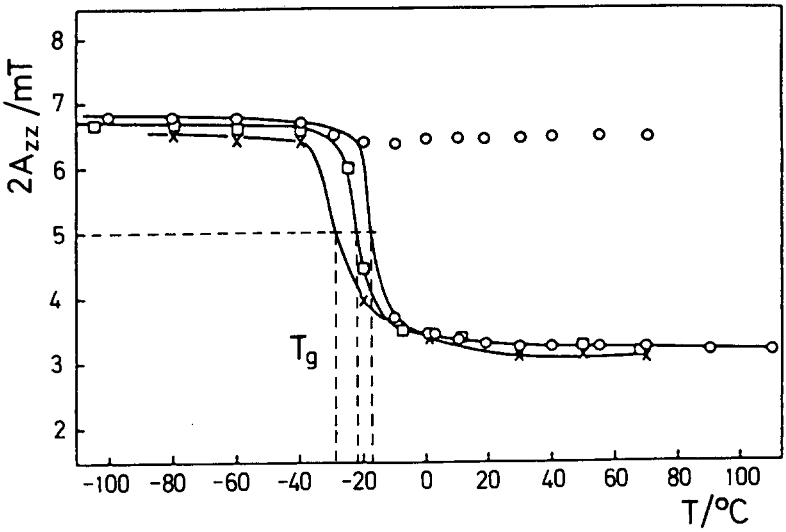

Figure 4. Extrema separation vs. temperature of natural rubber (○) and synthetic polyisoprenes PI-Ti (□) and PI-Li (x).

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